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ROPFECOTOSION IN DISTRIBUTION SYSTEMS

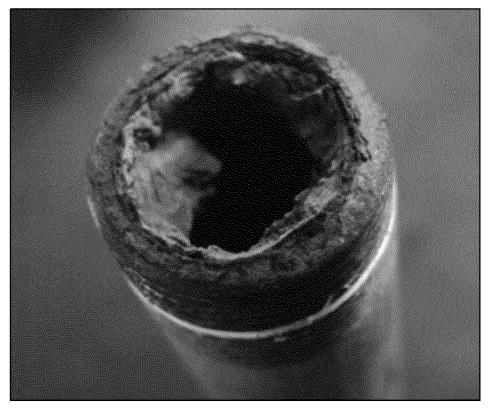
THIS LITERATURE REVIEW
SUMMARIZES THE RESULTS OF
ALMOST 300 PEER-REVIEWED
ARTICLES RELEVANT TO THE
DRINKING WATER INDUSTRY,
AND A REVIEW OF POTENTIAL
IMPLICATIONS OF UPCOMING
REGULATIONS FOR IRON
CORROSION IS ALSO INCLUDED.

ast-iron pipes have been used to transport potable water for more than 500 years (Gedge, 1992), and iron pipe corrosion has been a problem for just as long. AWWA estimates that it will cost US water utilities \$325 billion over the next 20 years to upgrade water distribution systems (AWWA,1999). This AWWAvalue is based on the US Environmental Protection Agency estimate of \$77.2 billion for service and replacement of transmission and distribution system lines over the next 20 years (Davies et al, 1997). The majority of distribution system pipes are composed of iron material: cast iron (38%), ductile iron (22%), and steel (5%) (AWWA,1996). Moreover, a 1997 survey of the 100 largest AWWA Research Foundation (AWWARF) member utilities found that "the most common distribution system problem is corrosion of cast-iron pipe" (Bray, 1997).

Although the body of literature on iron corrosion is quite large, most studies were conducted at experimental conditions inconsistent with the potable water distribution system environment (e.g., brine solutions, oil and gas pipelines, highly acidic conditions, or very high temperatures). The goal of this literature review is to summarize the results of several hundred peer-reviewed articles relevant to the drinking water industry.

Corrosion of iron pipes in a distribution system can cause three distinct but related problems. First, pipe mass is lost through oxidation to soluble iron species or iron-bearing scale. Second, the scale can accumulate as large tubercles that increase head loss and decrease water capacity. Finally, the release of soluble or particulate iron corrosion by-products to the water decreases its aesthetic quality and often leads to consumer complaints of "red water" at the tap. The water industry must be concerned with all three of these aspects of corrosion.

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Iron corrosion is an extremely complex process and can have several different manifestations, one of which is tuberculation as shown in this iron pipe.

IRON CORROSION MANIFESTS ITSELF IN DIFFERENT WAYS

Iron corrosion is an extremely complex process. Because of the large variability in distribution system conditions, a particular factor may be critical in one system but relatively unimportant in another system. Moreover, corrosion itself has several different manifestations and can be evaluated in many ways. Previous studies on iron pipe corrosion have focused on different aspects of iron corrosion. These include pipe degradation (measured by weight loss, oxygen consumption, or corrosion current), scale formation (measured by head loss or scale deposition), and byproduct release (measured by iron concentration, color, staining, turbidity, or number of customer complaints). Thus, it can be difficult to compare conclusions or theories from different studies. For example, one study found that head loss increased with increasing pH (Rice, 1947), whereas another study saw decreased iron by-product release at higher pH (Hidmi et al, 1994). Although both results could be explained by greater incorporation of corrosion by-products into the scale at higher pH, from a utility perspective the former result is "bad" whereas the latter is "good." Thus, this review carefully tracked which aspect of iron corrosion was studied (corrosion rate, scale formation, and iron by-product release). Table 1 provides a general overview of the expected effects of various factors on corrosion. The categories of "beneficial" and "detrimental" are used to describe how the effect would be perceived by the water utility or consumer. Further explanation and references are provided in the following sections.

SEVERAL WATER QUALITY PARAMETERS INFLUENCE CORROSION

Key water quality parameters that are expected to influence corrosion

include pH, alkalinity, and buffer intensity.

Role of pH. In the pH range 7 to 9, both weight loss (Stumm, 1960) and degree of tuberculation (Stumm, 1960; Larson & Skold, 1958b; Rice, 1947) were found to generally increase with increasing pH. In contrast, by-product release was decreased at higher pH (Hidmi et al, 1994). Again, this is consistent with increased corrosion by-products being incorporated into the scale layer. However, one study found that both weight loss and iron concentration decreased as pH was raised from 8.5 to 9.2 (Kashinkunti et al, 1999).

Alkalinity. Increasing alkalinity generally leads to lower weight loss (Kashinkunti et al, 1999; Hedberg & Johansson, 1987) and corrosion rate (Kashinkunti et al, 1999; Raad et al, 1998). Also, fewer customer complaints of red water were received when the alkalinity was maintained at higher values (Horsley et al, 1998).

Buffer intensity. Higher buffer intensity is often associated with increased alkalinity, although the two parameters are not exactly equivalent. However, their effect on iron corrosion seems to be similar. Several studies found that the maximum weight loss for cast-iron samples occurred at the minimum buffer intensity (pH 8.4) presumably because higher buffer intensity attenuates pH changes from corrosion reactions at anodic and cathodic areas (Clement & Schock, 1998; Van Der Merwe, 1988; Pisigan Jr. & Singley, 1987; Stumm, 1960). However, one study found the opposite effect-

TABLE 1 Summary of expected effects of various factors on iron corrosion

Potential Effect On . . .*

Factor	Corrosion Rate	Scale Buildup	By-product Release
pH increase		N = 3	ς _, +
Alkalinity increase	+	\ <u>-</u>	+
Buffer intensity increase	+	?	?
Dissolved oxygen increase	³ / ₂ -	· · ±	±
Kuch reaction	_	?	-
Calcite scale	+	· –	±
Siderite scale	+	?	+
Green rust scale	+	?	+
Langelier index	Should not be used	Should not be used	Should not be used
Larson index increase	±	±	± %
Disinfectant residual increase	i	?	-
Phosphate inhibitors	±	±	. ±
Silicates	+	+	±
Pipe age increase	+		+
Water velocity increase	· —	±	±
Stagnation time increase	?	?	_
Microbial activity	_	_	_
Temperatureincrease	_	?	_
Dissolved copper	_	?	?
Natural organic matter	+	+	_
"Free carbon dioxide"	_	?	_

^{*+-}beneficial effect, --detrimental effect, ±-mixed results, ?-not known

weight loss for iron coupons in stagnant water increased with increasing buffer intensity (Sander et al, 1996).

DISSOLVED OXYGEN (DO) PLAYS ROLE IN CORROSION

DO is an important electron acceptor in the corrosion of metallic iron:

$$Fe_{(metal)} + 0.5O_2 + H_2O$$

* $Fe^{+2} + 2OH^-$ (1)

DO can also play a role in the oxidation of ferrous iron (Fe⁺²) or iron scales, for example:

$$Fe^{+2} + 0.25O_2 + 0.5H_2O + 2OH^-$$

* $Fe(OH)_{3(s)}$ (2)

$$3FeCO_{3(s)} + 0.5O_2 * Fe_3O_{4(s)} + 3CO_2$$
 (3)

$$4Fe_3O_{4(s)} + O_2 * 6Fe_2O_{3(s)}$$
 (4)

In these equations, (s) denotes a solid precipitate.

Thus, oxygen concentration can have varying effects on iron corrosion. As expected, the corrosion rate increases with increasing DO (Gedge, 1992), although several studies found that iron release decreased with higher DO during stagnation (Sarin et al, 2000; Beckett et al, 1998). Effects on iron concentration and tuberculation may be mixed depending on the type of scale formed. Higher turbidity (a surrogate for iron concentration) was seen at lower oxygen saturation (Hulsmann et al, 1986), but it is also reported that water free of DO will not tuberculate (Baylis, 1953). DO is also responsible for the ability of buffering ions, including phosphates, to inhibit corrosion (Stumm, 1960; Cartledge, 1959; Pryor & Cohen, 1951). For example, in water with DO < 1 mg/L, solutions with phosphates had a higher corrosion rate compared

with waters with no phosphates; in water with 1–6 mg/L DO, this trend was reversed (Uhlig et al, 1955).

KUCH MECHANISM PROMOTES CORROSION IN LOW DO CONDITIONS

In the absence of oxygen, it is possible for previously deposited ferric scale (lepidocrosite, ¬-FeOOH) to act as an electron acceptor. This Kuch reaction produces ferrous iron and allows the corrosion reaction to continue even after DO is depleted (AWWARF & DVGW, 1996; Kuch, 1988):

$$Fe_{(metal)} + 2FeOOH_{(scale)} + 2H^+$$

* $3Fe^{+2} + 4OH^-$ (5)

A recent study (Sarin et al, 2000) found that iron corrosion still proceeded under anaerobic conditions despite the lack of lepidocrosite in the iron scale, indicating that the Kuch mechanism is not the only mechanism of iron release in deoxygenated waters.

SCALE COMPOSED OF MANY COMPOUNDS

The rate of corrosion of the iron metal has little relationship to the amount of iron that actually goes into the water, primarily because of the deposition of oxidized iron or other compounds into a scale that serves as a large reservoir of corrosion by-products. Iron scale is typically composed of many compounds and is thus very heterogeneous (Table 2). This scale layer may provide passivation (protection) by limiting the diffusion of oxygen to the metal surface and slowing the corrosion reaction. However, the scale will also contribute iron to the water. This includes both soluble species from scale dissolution as well as scale particles that detach from the surface. Unfortunately, it is difficult to model

this scale behavior. The scales are often poorly crystallized and heterogeneous, making solubility predictions very complex; even if solubility was understood, the water may be undersaturated because of kinetic or mass transfer limitations. Particulate detachment mechanisms are also complicated, depending on factors such as scale durability and adherence, water velocity, and temperature changes.

Clearly, scale formation is a complicated process that depends on a variety of physical and chemical conditions in each particular system. However, several well-known types of scale are postulated to affect iron corrosion.

Calcium carbonate. Precipitation of a thin layer of protective calcium carbonate (presumably calcite) was the earliest proposed method for controlling iron corrosion, and it was popular through at least the 1980s. Many articles have been dedicated to extolling the virtues of calcite layers (Flentje, 1961; Stumm, 1960; Larson, 1960; Stumm, 1959; Stumm, 1957; Larson & Skold, 1957; Stumm, 1956; Baylis, 1926; Tillmans & Heublein, 1912), and many others detail methods to achieve a perfect layer of protective calcite (see next section). However, few articles ever demonstrated a beneficial role for calcite in controlling iron corrosion.

Siderite. The siderite model postulates that the formation of reduced iron species, especially siderite (FeCO₃), provides a more protective scale than oxidized ferric scales such as goethite (FeOOH) or hematite (Fe₂O₃) (AWWARF & DVGW, 1996; Sontheimer et al, 1981). Siderite has been found in many iron scales (Smith et al, 1997; Fiksdal, 1995; Mishra et al, 1992; Feigenbaum et al, 1978a; Feigenbaum et al, 1978b;



"Red water," which is caused by the release of soluble or particulate iron corrosion by-products to the water, can result in customer complaints.

Stumm, 1960; Baylis, 1926). However, it is interesting to note a discrepancy regarding siderite in studies of pure iron in high-carbonate solutions (not drinking water). Two such studies concluded that siderite was the key to forming a protective scale (Simpson & Melendres, 1996; Blengino et al, 1995). However, two others with similar conditions found that the formation of siderite destroyed the protective nature of other iron oxide films (Valentini et al, 1985; Ikeda et al, 1984).

Green rust. "Green rust" is the generic name given to iron compounds containing both ferrous and ferric iron, as well as other ions such as carbonate, chloride, and sulfate (Genin et al, 1998; Simon et al, 1997). Green rusts have been identi-

fied in the corrosion products on iron and steel (Tuovinen et al, 1980; McGill et al, 1976), and they may act similarly to siderite and form a dense protective film (AWWARF & DVGW, 1996).

CORROSION INDEXES DO NOT SOLVE PROBLEMS

Calcite indexes. The Langelier index (Merrill & Sanks, 1979; Merrill & Sanks, 1978; Merrill & Sanks, 1977a; Merrill & Sanks, 1977b; Langelier, 1936) (also called the saturation index [SI]) has been improperly applied as the cure-all method for solving corrosion problems since it was first proposed in 1936. Although this method was successful at some utilities, it was by no means a universal method for controlling corro-

sion. To his credit, Langelier never intended the index to be used in this manner and even pointed out its limitation in certain waters (Langelier, 1946). Several other studies also found that the SI had no correlation with corrosion rate (Pisigan Jr. & Singley, 1987; Piron et al, 1986; Singley, 1981; Larson & Sollo, 1967; Stumm, 1960). Despite proposed modifications to the Langelier index (Pisigan Jr. & Singley, 1985a; Pisigan Jr. & Singley, 1985b; Schock, 1984) and its continued use by many utilities, the AWWA manual on corrosion states, "In light of much empirical evidence contradicting the presumed connection between the LI [Langelier index] and corrosion, this practice should be abandoned" (AWWARF & DVGW, 1996). Likewise, other calcite indexes that have been proposed have only limited use in corrosion control. These indexes include the Ryznar index (Ryznar, 1944), aggressiveness index (Millette et al, 1980), momentary excess (Dye, 1958), driving force index (Rossum & Merrill, 1983), and calcium carbonate precipitation potential (Merrill & Sanks, 1978; Merrill & Sanks, 1977a; Merrill & Sanks, 1977b). See Rossum & Merrill (1983) for a review of all indexes.

Larson index. The studies of Larson (Larson, 1975; Larson & Skold, 1958a; Larson & Skold, 1957) found that the ratio of chloride and sulfate to bicarbonate was important, as expressed in the Larson index:

Larson index =
$$\frac{2[SO_4]_{L} + [CI]}{[HCO_3]}$$
 (6)

A higher index indicates a more corrosive water. Several studies qualitatively confirmed these results (although they never directly tested the accuracy of the Larson index) by

reporting that increased chloride (Veleva et al, 1998; Hedberg & Johansson, 1987) and sulfate (Veleva et al, 1998; Riddick, 1944) caused increased weight loss. Another article proposed that the presence of sulfate or chloride in the water leads to iron chloride and/or iron sulfate complexes in the iron scale that increase ferrous iron diffusion, causing increased iron concentrations (Elzenga et al, 1987). However, several other studies found contradictory effects, including that sulfate inhibits dissolution of iron oxides, leading to lower iron concentrations (Bondietti et al, 1993), the presence of sulfate and chloride caused a more protective scale on steel surfaces (Feigenbaum et al, 1978a), and that sulfate and chloride concentrations had no effect on weight loss of cast iron (Van Der Merwe, 1988; Piron et al, 1986).

DISINFECTANT RESIDUALS CAN INCREASE CORROSION RATES

In general, disinfectant residuals increase corrosion rates (Pisigan Jr. & Singley, 1987; Hoyt et al, 1979). Monochloramine was found to be less aggressive than free chlorine (Treweek et al, 1985). However, if the corrosion is microbially induced, higher disinfectant residuals may decrease corrosion (LeChevallier et al, 1993).

PHOSPHATE INHIBITORS PLAY A MIXED ROLE

Phosphate-based inhibitors have been added to drinking water since the early 1900s. Phosphates were first used to prevent excessive calcite precipitation (Hoover & Rice, 1939). The mechanism of this "threshold treatment" was thought to be the sorption onto calcium carbonate nuclei, which prevented the calcite crystals from growing outside of the

colloidal range (Hatch & Rice, 1939). Researchers later discovered that these phosphates could sometimes prevent iron corrosion and red water problems.

Polyphosphates. Condensed chain phosphates, known generally as polyphosphates, were the first phosphorus compounds to be used in corrosion control. The original polyphosphate, known as sodium hexametaphosphate, glassy phosphate, or metaphosphate glass, had the approximate chemical formula Na₂₂P₂₀O₆₁. Numerous studies found that polyphosphate could prevent corrosion and/or control red water (Facey & Smith, 1995; Williams, 1990; Huang, 1980; McCauley, 1960a; McCauley, 1960b; Hamilton & Flentje, 1958; Illig Jr., 1957; Larson, 1957; Uhlig et al, 1955; Lamb & Eliassen, 1954; Parham & Tod, 1953; Hatch, 1952; Raistrick, 1952; Barbee, 1947; Rice, 1947; Cohen, 1946; Pallo, 1946; Hatch & Rice, 1945a; Hatch & Rice, 1945b; Hatch & Rice, 1940). Corrosion prevention and red water control are in fact two very different phenomena, but this distinction was sometimes overlooked in these studies. Many reported beneficial results for corrosion are simply because of stabilization of iron particles, causing a decrease in the visual observation of "red water." This led researchers to claim that iron by-product release had decreased, when in reality the iron concentration and even the corrosion rate might have increased.

The theory of polyphosphate corrosion prevention, if discussed at all in these articles, varies widely. Some researchers claimed that the polyphosphate adsorbed onto the iron surface to form a protective film (Hatch & Rice, 1945b). Other studies have stressed the importance of calcium in polyphosphate effective-

Name	Chemical Formula	Iron Oxidation Sta
Ferrous hydroxide	Fe(OH) ₂	S III
Ferric hydroxide	Fe(OH) ₃	. 111
Wustite	FeO	i II
Goethite	FeOOH	<u>,</u> III
Akaganeite	-FeOOH	<u> </u>
Lepidocrosite	¬ -FeOOH	111
Hematite	-l-Fe₂O₃	III
Maghemite	¬-Fe ₂ O ₃	III
Magnetite	Fe ₃ O ₄ (FeO·Fe ₂ O ₃)	II and III
Ferric oxyhydroxide	FeO _x (OH) _{3–2x}	III
Siderite	FeCO ₃	II
Iron hydroxycarbonate	Fe _x (OH) _y (CO ₃) _z	Ш
"Green rust"	$Fe(III)_{x1}Fe(II)_{x2}(OH)_y(CO_3,SO_4)_z$	II and III
Vivianite	Fe ₃ (PO ₄) ₂ · 8H ₂ O	II
Strengite	FePO ₄	Ш
Schrebersite	Fe₄P	Not known

ness (Kamrath et al, 1993; Rangel et al, 1992; Bailey, 1980; Huang, 1980; Murray, 1970; Kleber, 1965; McCauley, 1960a; McCauley, 1960b; Uhlig et al, 1955; Parham & Tod, 1953; Hatch, 1952; Raistrick, 1952; Green, 1950; Barbee, 1947; Hatch & Rice, 1945a; Hatch & Rice, 1945b; Hazel, 1942; Hatch & Rice, 1939). This is believed to be because of formation of a thin calcite layer made protective by the adsorption of polyphosphate ions (Morris Jr., 1967; McCauley, 1960a; McCauley, 1960b; Raistrick, 1952; Evans, 1946). Other studies have stressed the importance of flow conditions on the efficacy of polyphosphate action (see later section).

Orthophosphate. Unlike polyphosphates, orthophosphates are added for scale formation but not for iron sequestration (Wagner, 1992; Benjamin et al, 1990; Boffardi, 1988; Wagner & Kuch, 1984; Huang, 1980; Pryor & Cohen, 1951). One often overlooked fact is that poly-

phosphates revert to orthophosphate with time (Green, 1950), so the results of many polyphosphate studies could be confounded by the presence of orthophosphate.

Bimetallic (zinc) phosphate. In the 1960s, manufacturers began blending polyphosphates and orthophosphates with 5-25% zinc to form bimetallic phosphates, claiming either that the presence of zinc accelerated polyphosphate film formation or that a zinc orthophosphate or zinc polyphosphate film was superior to regular phosphate films for inhibiting corrosion. These compounds were reported to decrease corrosion compared with regular polyphosphates or orthophosphates (Bancroft, 1988; Swayze, 1983; Bailey, 1980; Mullen & Ritter, 1980; Mullen & Ritter, 1974; Murray, 1970; Powers et al, 1966; Kleber, 1965). However, several studies found no benefit of zinc phosphates compared with regular phosphates (McNeill & Edwards, 2000; Volk et al, 2000; Malcolm

Pirnie, 1998; Williams, 1990; Wagner & Kuch, 1984; Swayze, 1983; Huang, 1980). Moreover, recent concerns about zinc loading to wastewater plants has somewhat curtailed the usage of these zinc phosphates (AWWARF & DVGW, 1996).

Other mechanisms. Several other phosphate effects are traditionally not considered in the context of pipe corrosion. Phosphate sorption may restabilize iron scales as colloids (Hazel, 1942). A recent study found that orthophosphate reduced the size and increased the surface charge of iron colloids (Lytle & Snoeyink, 2000). Polyphosphate has been shown to induce ligand-promoted dissolution of iron oxides, leading to higher iron concentrations in water (although very high phosphate concentrations may actually cause a decrease in iron concentration [Lin & Benjamin, 1990]). Orthophosphate can either inhibit or enhance ligand-promoted dissolution depending on pH (Deng & Stumm, 1994; Bondietti et al, 1993). Orthophosphate also dramatically decreases reductive dissolution of iron oxides (Biber et al, 1994).

SILICATES DISPERSE IRON PARTICLES

Silicate compounds were first used as a coagulation aid because of their ability to adsorb onto particles and decrease surface charge (Stumm et al, 1967; Baylis, 1937). These properties were soon applied to sequestration (dispersion) of iron particles in distribution systems (Schock et al. 1998; Robinson et al, 1992; Browman et al, 1989; Dart & Foley, 1972; Dart & Foley, 1970). An early study (Riddick, 1944) found that natural silica present in the water was concentrated in the relatively protective iron scale. Addition of silicate-based inhibitors has also been found to

The role of biological activity in a water pipe can be mixed but is generally considered to be detrimental to most aspects of iron corrosion.

reduce iron corrosion rate (Rompre et al, 1999; Raad et al, 1998; Williams, 1990). Finally, silicates are reported to decrease the oxidation of ferrous iron because ferrous iron diffusion through the silicate film is slower than through iron oxide scale (Hadad & Pizzo, 1992).

Silicates appear to form a self-limiting film on the corroded iron surface that will break down if silica dosing is stopped. It has been proposed that the metal must already be somewhat corroded because the protective film must consist of ferric oxide and silicate (AWWARF & DVGW, 1996); similarly, iron must be oxidized in order to be sequestered by the silicate (Schock et al, 1998; Robinson et al, 1992; Dart & Foley, 1972). Addition of silicates can also raise the pH, which is generally beneficial toward iron corrosion. Silicates are naturally present in many waters and may have effects similar to those of added silicate inhibitors.

PIPE AGE CAN DRAMATICALLY AFFECT CORROSION

The length of time the pipe has been aged dramatically affects its corrosion. In general, both iron concentration and the rate of corrosion increase with time when a pipe is first exposed to water, but both are then gradually reduced as the scale builds up. However, the location of this "cross-over" point varies widely with water quality and other conditions.

MIXED RESULTS AVAILABLE ON EFFECT OF WATER VELOCITY

There are very mixed results for the effect of flow velocity (see Eliassen et al (1956) and Pallo (1946) for a review). It is thought that two factors are dominant: increased flow provides more oxygen for the corrosion reaction, but it can also hasten the precipitation of a protective layer. For example, a study of mild steel found that the weight loss increased with increasing water velocity when the DO was saturated (Gedge, 1992; Pisigan Jr. & Singley, 1987). However, other studies found a more dense protective layer at higher water flow rates (Fiksdal, 1995). Also, if the velocity is very high, the water can scour away the protective scale.

There is anecdotal evidence that phosphate inhibitors perform poorly at low flow or stagnant conditions (Rompre et al, 1999; Larson, 1957; Cohen, 1946; Hatch & Rice, 1945b; Hatch & Rice, 1940), and several studies found that phosphate inhibitors had no effect or actually increased iron corrosion under such conditions (McNeill & Edwards, 2000; Maddison & Gagnon, 1999; Rice, 1947; Pallo, 1946).

STAGNATION TIME MAY INCREASE CONCENTRATIONS OF IRON

Iron concentrations were shown to increase with longer stagnation times (Sarin et al, 2000; Beckett et al, 1998). One study from the Netherlands (van Rijsbergen et al, 1998) found that turbidity in a castiron distribution system peaked during the night, then decreased in the early morning as demand increased and stagnation time decreased.

BIOLOGICAL ACTIVITY ALSO IMPORTANT

Microorganisms are present in many distribution systems (Holden et

al, 1995; LeChevallier et al, 1993; De Araujo-Jorge et al, 1992; Emde et al, 1992; Smith & Emde, 1992; Victoreen, 1984; Allen et al, 1980; Lee et al, 1980; Tuovinen et al, 1980; O'Conner et al, 1975; Larson, 1939), and they can influence iron corrosion in a number of ways. Bacteria have been found in iron tubercles (Emde et al, 1992; Smith & Emde, 1992; Allen et al, 1980; Tuovinen et al, 1980; Victoreen, 1974). Growth of a bacterial biofilm on a pipe wall may serve as a barrier to corrosion (Abernathy & Camper, 1998; O'Conner et al, 1975), but biofilms can also produce a differential aeration cell, leading to localized changes in oxygen concentration and electrical potential (Lee et al, 1980). The biopolymers in the biofilm may also uptake soluble metals (Tuovinen et al, 1980). Various bacteria can affect iron speciation by reducing Fe⁺³ or oxidizing ferrous iron (Nemati & Webb, 1997; Chapelle & Lovley, 1992; Okereke & Stevens Jr., 1991; Kovalenko et al, 1982; Denisov et al, 1981; Shair, 1975). Bacteria may also consume oxygen (Larson, 1939), cause localized pH gradients (Tuovinen et al, 1980), and produce corrosive metabolites such as hydrogen sulfide (De Araujo-Jorge et al, 1992; Tuovinen et al, 1980) or iron phosphide (Iverson, 1998; Hamilton, 1985; Iverson et al, 1985; Iverson, 1984; Iverson & Oldon, 1983; Iverson, 1981; Iverson, 1968). Thus, the role of biological activity in a water pipe can be mixed but is generally considered to be detrimental to most aspects of iron corrosion. In cases in which such activity is dominant, it is not surprising that biocides such as chlorine effectively reduce overall corrosion problems despite their oxidative properties.

TEMPERATURE'S EFFECTS OFTEN OVERLOOKED

The effect of temperature on iron corrosion is often overlooked. Many parameters that influence corrosion can vary with temperature. These parameters include DO solubility, solution properties (e.g., viscosity and ion mobility), ferrous iron oxidation

rate, thermodynamic properties of iron scale (leading to formation of different phases or compounds), and biological activity. Moreover, heterogeneous iron scale formed on pipes may have large differences in physical properties such as scale density (as described by the Pilling-Bedworth ratio) and coefficients of thermal expansion (Schutze, 1997). If the scale is exposed to temperature gradients or cycling, these differences

can cause mechanical stresses in the scale, leading to spalling or crack formation.

Only a few studies have examined the role of different temperatures in distribution system corrosion. In one study, iron samples held at 13°C had lower weight loss compared with samples at 20°C (Fiksdal, 1995). Other studies found lower iron concentrations (Volk et al, 2000) and fewer customer complaints of red

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water (Horsley et al, 1998) during the colder winter months. Finally, two pilot-scale studies saw peaks in turbidity (Smith et al, 1998) and metal concentrations (MacQuarrie et al, 1997) that appeared to correlate with temperature changes.

OTHER COMPOUNDS HAVE EFFECTS

Dissolved copper. Two studies found that concentrations of dissolved copper as low as 0.01 mg/L catalyzed

iron corrosion rates (Cruse, 1971; Hatch, 1955).

Natural organic matter (NOM). Several studies (Lind Johansson, 1989; Sontheimer et al, 1981; Larson, 1966) found that NOM decreased the corrosion rate of both galvanized steel and cast iron. NOM was also found to encourage a more protective scale (Campbell & Turner, 1983) and alter the redox chemistry by reducing Fe⁺³ colloids to soluble fer-

rous iron (Deng & Stumm, 1994). However, NOM can complex metal ions (AWWARF & DVGW, 1996), which may lead to increased iron concentrations.

"Free carbondioxide." Several studies stressed the importance of "free carbon dioxide," which is the sum of carbonic acid and dissolved carbon dioxide. These studies found that the free carbon dioxide forms surface complexes on the iron oxide, increas-

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ing the solubility of ferrous iron and thus increasing iron concentration and corrosion rates (Sander et al, 1997; Sander et al, 1996; Sander et al, 1995; Ahlberg, 1995).

MAGNETIC PROPERTIES MIGHT HAVE EFFECTS

Some iron oxides, such as magnetite, are magnetic, whereas others such as hematite are not. One final interesting theory is that pre-

cipitated ferric scale is attracted back to the pipe surface by magnetic force, so the amount of scale built up depends on its magnetic properties (Baylis, 1953).

UPCOMING REGULATIONS MAY HAVE IMPACT ON IRON CORROSION

The drinking water industry faces numerous impending or recently promulgated regulations. Implementation of these new regulations may require significant changes to treatment processes and finished water quality, thereby creating the potential for secondary effects on iron corrosion (Siebel, 1998).

Lead and Copper Rule (LCR). The LCR (USEPA, 1991), first implemented in 1991, requires utilities to control lead and copper levels in tap water. In order to comply with the LCR, most utilities either changed their finished water quality or began

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dosing phosphate inhibitors. Typical water quality adjustments are raising pH and lowering dissolved inorganic carbon. According to Table 1, raising pH is detrimental to iron corrosion rate and scale buildup but can reduce the release of by-products.

Many utilities began adding phosphate inhibitors to meet the LCR, often without regard to how the inhibitors would affect iron corrosion. In fact, from 1992 to 1994 the percentage of large utilities dosing inhibitors doubled from 30 to 60% (Edwards et al, 1999) and may be even higher today. Although these phosphate inhibitors can be effective in decreasing lead and copper corrosion under some conditions, they can also be quite detrimental to iron corrosion (McNeill & Edwards, 2000).

Disinfectants/Disinfection By-products Rule (D/DBPR). Implementing the D/DBPR (USEPA, 1998b) can affect iron corrosion because of changes associated with disinfection and increased organic matter removal. As discussed earlier, decreased disinfectant residuals generally decrease corrosion rates. However, decreased disinfectant residual may increase corrosion if it is related to microbial

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activity. Many utilities may also change to a different disinfectant (e.g., from chlorine to chloramine), which can also affect iron corrosion.

The second aspect of the D/DBPR is the requirement for increased removal of organic matter (as measured by total organic carbon [TOC]) through enhanced coagulation or enhanced softening. Organic matter is thought to be beneficial for iron corrosion rate and scale buildup but detrimental to byproduct release, so the overall effect of increased TOC removal is unclear. Other potential effects of enhanced treatment have been documented (AWWA Government Affairs Office, 1998). Briefly, enhanced coagulation can be associated with lower pH and alkalinity and higher sulfate and chloride concentrations because of increased coagulant doses. Enhanced softening may be associated with higher pH, lower alkalinity, and decreased hardness. According to Table 1, each of these factors may have mixed consequences for iron corrosion.

Enhanced Surface Water Treatment Rule (ESWTR), Ground Water Rule (GWR), and Total Coliform Rule (TCR). In contrast to the D/DBPR, the primary concern for utilities trying to meet the ESWTR (USEPA, 1998a),

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GWR, or TCR (USEPA, 1989) will be increased disinfection and disinfectant residual requirements. In addition, the TCR may require changes in circulation and flow patterns in the distribution system in order to decrease "dead ends." This may be beneficial to corrosion, because these dead-end areas are often the source of iron corrosion problems because of low flow conditions and decreased DO.

SUMMARY

Iron pipe corrosion is extremely complicated and is affected by practically every physical, chemical, and biological parameter in water distribution systems. This work provides a summary of key factors that utilities must evaluate in order to mitigate iron corrosion problems. Utilities should also consider potential secondary impacts on corrosion

because of compliance efforts for new regulations.

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If you have a comment about this article, please contact us at <journal@awwa.org>.

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